

# Effectiveness of Organics and Nitrogen Removal from Municipal Landfill Leachate in Single- and Two-Stage SBR Systems

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Received: 3 June 2003

Accepted: 20 January 2004

## Abstract

The efficiency of organics and nitrogen removal from municipal landfill leachate in activated sludge operated as single and two-stage SBR were investigated. Leachate from mature landfills are characterized by high N/COD ratio ( $> 0.5$ ). In single activated sludge system at the hydraulic retention time (HRT) 3d and at methanol dosage 8 mg COD/mg  $N_{NO_3}$  complete ammonium nitrogen removal was obtained. Ammonium concentration in the effluent was 0.15 mg  $N_{NH_4}/dm^3$  and nitrate — 23.5 mg  $N_{NO_3}/dm^3$ . At the hydraulic retention time 2d, nitrate nitrogen concentration in the effluent decreased to 2.79 mg  $N_{NO_3}/dm^3$ . The concentration of ammonium nitrogen was 0.35 mg  $N_{NH_4}/dm^3$ . However, a sporadically high concentration of ammonium appears. In a two-stage SBR system, HRT 2d was sufficient to achieve complete nitrification. In the effluent ammonium and nitrate concentrations were 0.08 mg  $N_{NH_4}/dm^3$  and 320 mg  $N_{NO_3}/dm^3$ , respectively. In the anoxic reactor at HRT 1d and methanol dosage 3.6 mg COD/mg  $N_{NO_3}$  complete denitrification was obtained.

Raw leachate contained specific hazardous organics, among others BTEX (175.8  $\mu g/dm^3$ ), chloroorganics (55.7  $\mu g/dm^3$ ), chlorobenzenes (0.75  $\mu g/dm^3$ ) and PAHs (1.97  $\mu g/dm^3$ ). In the effluent from single and two-stage SBR systems chloroorganics and chlorobenzenes were not detected. BTEX and PAH concentrations in the effluent from two-stage system were adequately 2-fold and 2.1-fold lower in comparison to a single one. Besides, the effluent from two-stage SBR systems did not contain benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene and indeno(1,2,3-cd)pyrene.

**Keywords:** landfill leachate, activated sludge, sequencing batch reactor, specific organic compounds, nitrification, denitrification, methanol.

## Introduction

Leachate from landfills are potentially environmental hazards as surface and groundwater contamination. Recently, substantial research has been conducted on organic and nitrogen compound removal from leachate. One criteria of choice of leachate treatment methods is the leachate composition, which

depends on the type of deposited wastes and landfill age.

In the first years of landfill operation, in leachate-free volatile fatty acids represented the largest group of organics, and this fraction showed a rapid decrease with increasing age of the landfill. The most stable group of organics with increasing age was a fulvic-like material with a relatively high carboxyl and aromatic hydroxyl group density [1, 2, 3, 4]. Specific organic compounds identified in the leachate are BTEX, phthalates, furans, pesticides, polycy-

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Table 1. Composition of raw leachate.

Leachate constituent	Concentration	
	series 1	series 2
Chemical oxygen demand (COD) (mgO <sub>2</sub> /dm <sup>3</sup> )	680	757
Biochemical oxygen demand (BOD <sub>5</sub> ) (mgO <sub>2</sub> /dm <sup>3</sup> )	112	132
Ammonium nitrogen (mgN <sub>NH4</sub> /dm <sup>3</sup> )	312	362
Total nitrogen (mgN <sub>og</sub> /dm <sup>3</sup> )	344	397

clic aromatic hydrocarbons (PAHs), halogenated aromatics and benzene- and naphthalenesulfonates [5, 6, 7].

Ammonium nitrogen concentration increased in leachate along with landfill age. It was observed that in leachate from mature landfills this content was in the range of 2000-3000 mg N<sub>NH4</sub>/dm<sup>3</sup> [8, 9, 10].

The main applicable methods of landfill leachate treatment are biological, chemical, membrane separation and thermal treatment processes. Removal organics (as BOD<sub>5</sub> and COD) from landfill leachate has been studied by many investigators [11, 12, 13]. However, the removal of specific organics from leachate is not widely known. Biological methods including aerobic and anaerobic processes have been shown to be very effective for the treatment of landfill leachate which had high BOD/COD ratio. For treatment leachate with the low COD/N ratio nitrification/denitrification processes was usually suggested. Nitrification was studied in reactors with activated sludge containing plastic carrier material as small cubes of macroporous cellulose or tubes made of polyethylene with an addition of ammonium chloride [14] or in trickling filter [15]. Commonly used appliances for nitrogen removal are moving-bed biofilm process, based on the use of small, free-floating polymeric (polyurethane) elements, while biomass is being grown and attached as biofilm on the surface of these porous carriers [16]. Acetate, methanol, glucose, maltose and high strength wastes such as brewer's yeast waste have been used as external carbon source in the denitrification of landfill leachate when COD/N ratio was lower than the optimum one [17, 18].

From the literature data result that as for municipal sewage, especially at small wastewater treatment plants, a high nitrogen removal effectiveness is obtained in sequencing batch reactors (SBR) [19, 20]. According to Andreottola et al., [21] SBR systems applied to nitrogen removal from industrial wastewater offer various advantages, including: minimal space requirements, ease of management and possibility of modifications during trial phases through on-line control of the treatment strategy. In the accessible literature there are not a lot of reports concerning nitrification and denitrification in SBR reactors during leachate treatment.

The data concerning specific organics removal from leachate are uncommon and incomplete.

The aim of this study was to investigate treatment efficiency of leachate from mature landfill in SBR system. In the experiment a single and two-stage sludge system were tested. Removal efficiency of organics (as COD and BOD<sub>5</sub>) and 44 other specific organic compounds including BTEX, chloroorganics, chlorobenzenes, PAHs and PCBs were analyzed. Nitrogen removal effectiveness was tested at different hydraulic retention time in SBR reactors. In single and two-stage systems methanol was used as an external carbon source. In both systems a comparison of methanol doses was carried out.

## Materials and Methods

### Leachate Feed

The leachate used in this study was collected from municipal landfill located in Wysieka (near Bartoszyce), which has been in operation since 1996. The leachate composition was typical for a mature landfill, with low biodegradable carbonaceous matter and high concentrations of ammonium. Leachate characterizations are presented in Table 1.

In raw leachate nearly 30 of 44 analyzed specific organic compounds were identified in the leachate. Among these compounds were BTEX, chloroorganics, chlorobenzenes, PAHs and PCBs. Concentrations of the pollutants were usually low (< 0.3 µg/dm<sup>3</sup>) except for toluene, ethylbenzene, xylene and trichloromethane, which were measured in concentrations ranging from 31.4 µg/dm<sup>3</sup> to 82.7 µg/dm<sup>3</sup> (Tab. 2).

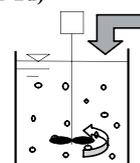
### Process Configuration and System Design

The single- (simultaneous nitrification/denitrification) and two-stage (post denitrification) SBR systems were used for landfill leachate treatment. Reactors were operated at room temperature. External carbon source in the form of methanol was added to achieve nitrogen elimination.

#### Single SBR System (Simultaneous Nitrification/Denitrification System) – Series 1

Two identical SBR reactors were operated in a 24-h cycle mode, at hydraulic retention time (HRT) 3d (SBR 1 N-D)

#### SBR 1 N-D (HRT 3d) SBR 2 N-D (HRT 2d)



feed (raw leachate + methanol)

cycle – 24h  
feed – 0.25h  
mixing – 3h  
aeration – 17.5h  
settle – 3h  
decant – 0.25h

Fig 1. Duration phases time in single SBR system in SBR 1 N-D and SBR 2 N-D (series 1).

Table 2. Specific hazardous organics compounds identified in raw leachate.

BTEX ( $\mu\text{g}/\text{dm}^3$ ) (sum)	<b>175.8</b>
• benzene	0.6
• toluene	31.4
• ethylbenzene	61.1
• xylene	82.7
Chloroorganics ( $\mu\text{g}/\text{dm}^3$ ) (sum)	<b>55.7</b>
• dichloroethane	0.3
• dichloroethene	0.7
• trichloromethane	54.7
• bromochloromethane	n.d.
• tetrachloromethane	n.d.
Chlorobenzenes ( $\mu\text{g}/\text{dm}^3$ ) (sum)	<b>0.75</b>
• chlorobenzene	0.24
• 1,3-dichlorobenzene	0.03
• 1,4-dichlorobenzene	0.27
• 1,2-dichlorobenzene	0.07
• 1,3,5-trichlorobenzene	n.d.
• 1,2,4-trichlorobenzene	n.d.
• 1,2,3-trichlorobenzene	0.06
• 1,2,3,5-tetrachlorobenzene	n.d.
• 1,2,4,5-tetrachlorobenzene	n.d.
• 1,2,3,4-tetrachlorobenzene	n.d.
• pentachlorobenzene	n.d.
• hexachlorobenzene	0.08
PAHs ( $\mu\text{g}/\text{dm}^3$ ) (sum)	<b>1.97</b>
• naphthalene	0.142
• acenaphthalene	0.112
• acenaphthene	0.116
• fluorene	0.226
• phenanthrene	0.284
• anthracene	0.057
• fluoranthene	0.258
• pyrene	0.284
• benzo(a)anthracene	0.125
• chrysene	0.121
• benzo(b)fluoranthene	0.117
• benzo(k)fluoranthene	0.036
• benzo(a)pyrene	0.045
• indeno(1,2,3-cd)pyrene	0.044

• dibenzo(a,h)anthracene	n.d.
• benzo(g,h,i)perylene	n.d.
PCBs ( $\mu\text{g}/\text{dm}^3$ ) (sum)	<b>0.001</b>
• 2,4,4'-trichlorobiphenyl (PCB 28)	n.d.
• 2,2',5,5'-tetrachlorobiphenyl (PCB 52)	n.d.
• 2,2',4,5,5'-pentachlorobiphenyl (PCB 101)	n.d.
• 2,3',4,4',5-pentachlorobiphenyl (PCB 118)	n.d.
• 2,2',4,4',5,5'-heksachlorobiphenyl (PCB 153)	n.d.
• 2,2',3,4,4',5-heksachlorobiphenyl (PCB 138)	0.001
• 2,2',3,4,4',5,5'-heptachlorobiphenyl (PCB 180)	n.d.

n.d. - not detected

and 2d (SBR 2 N-D) in parallel. The total volume of each reactor was 6  $\text{dm}^3$ . The procedures of reactor operation such as feed (0.25h), mixing (3h), aeration (17.5h), settlement (3h) and decanting (0.25h) were controlled automatically by timers (Fig. 1).

### Two-Stage SBR System (Post Denitrification System) – Series 2

The laboratory two-stage system contained aerobic (SBR-N) and anoxic (SBR-D) SBR reactors.

The SBR-N reactor was operated in a 24-h cycle mode, at 0.25, 20.5, 3 and 0.25 hours for the feed, aeration, settlement and decanting, respectively. Hydraulic retention time (HRT) 2d was maintained for organics removal and nitrification. The SBR-D reactor was a purely denitrifying reactor. The SBR-D reactor was operated at 1d HRT in a 12-h cycle mode. Duration phases time was 0.25, 10, 1.5 and 0.25 hours for the feed, mixing, settlement and decanting, respectively (Fig. 2).

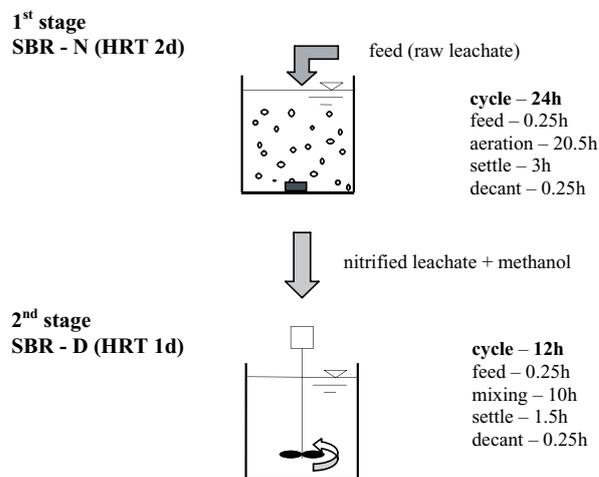


Fig. 2. Duration phase times in two-stage SBR system (series 2).

## Methanol Dosage

### Single SBR System – Series 1

From the stoichiometric anoxic respiration, it can be calculated that 1g  $N_{NO_3}$  equals 2.86 g  $O_2$  in oxidation-reduction reactions. However, according to Wanner [22], in municipal sewage treatment with pre-denitrification the actual consumption of readily biodegradable substrates for complete denitrification of 1g  $N_{NO_3}$ , expressed as COD units, is estimated to be about 8.

In order to calculate methanol demand in single SBR system concentration of internal carbon source (as COD) and concentration of nitrogen oxidized to nitrates have to be determined.

We recorded that:

- the concentration of organics used by denitrifiers as carbon source responds the value of  $BOD_5$ . In raw leachate organic compounds concentration, expressed as COD and  $BOD_5$  was adequately 680  $mgO_2/dm^3$  and 112  $mgO_2/dm^3$  ( $BOD_5/COD = 0.16$ ). It was assumed that  $f = 0.16$ ,
- the amount of ammonium used for biomass synthesis was calculated from the formula (1) according to Wojnowska-Baryła, Stachowiak [23]:

$$C'_{N-NH_4, syn} = (Y_{obs} \cdot (C_0 - C_e) \cdot Z_N) \quad (1)$$

where:

- $C'_{N-NH_4, syn}$  – ammonium amount used for biomass synthesis during SBR cycle ( $mg N_{NH_4}/dm^3$ ),
- $Y_{obs}$  – observed biomass yield coefficient ( $mg VSS/mg COD$ ),
- $C_0$  – organics concentration (COD) in leachate at the beginning of the SBR cycle ( $mgO_2/dm^3$ ),
- $C_e$  – organics concentration (COD) in effluent ( $mgO_2/dm^3$ ),
- $Z_N$  – nitrogen content in dry mass of activated sludge ( $mgN/100mg VSS$ ),

The observed biomass yield coefficient  $Y_{obs}$  and nitrogen content in dry mass of activated sludge  $Z_N$  was calculated by Kulikowska [24].

Then the ratio of organic compounds concentration and ammonium may be described as follows:

$$\frac{C_{0,m} + 0.16 \cdot C_0}{C_{0,NNH_4} - C'_{NNH_4, syn}} = 8 \quad (2)$$

Methanol dosage  $C_{0,m}$  was calculated after conversion to the formula (3):

$$C_{0,m} = (8 \cdot (C_{0,NNH_4} - C'_{NNH_4, syn})) - 0.16 \cdot C_0 \quad (3)$$

where:

- $C_{0,m}$  – methanol concentration (COD) at the beginning of the SBR cycle ( $mgO_2/dm^3$ ),
- $C_0$  – organics concentration (COD) in leachate at the beginning of the SBR cycle ( $mgO_2/dm^3$ ),

- $C_{0,NNH_4}$  – ammonium concentration at the beginning of the SBR cycle ( $mg N_{NH_4}/dm^3$ ),
- $C'_{N-NH_4, syn}$  – ammonium amount used for biomass synthesis during SBR cycle ( $mg N_{NH_4}/dm^3$ ).

### Two-Stage SBR System – Series 2

In our experiment biodegradable organics concentration in nitrified leachate was low ( $BOD_5 < 8 mgO_2/dm^3$ ), which could be omitted at methanol dosage calculation. In post-denitrification (SBR-D), stoichiometric methanol dosage ( $1.9 mg CH_3OH/mg N_{NO_3}$ ) increased by the coefficient *consumptive ratio* was approved, which responds to  $2.47 mg CH_3OH/mg N_{NO_3}$  or, expressed as COD -  $3.6 mg O_2/mg N_{NO_3}$ .

### Analytical Method

The daily measured parameters were COD and  $BOD_5$  (as unspecific indicators express content of organic compounds), ammonium, nitrate and nitrite. The analyses were carried out according to the methodology described by Hermanowicz et al. [25].

In raw leachate and in the effluents from single (SBR 2 N-D) and two-stage system (SBR-D) double analyses of hazardous organic compounds such as: BTEX (according to PN-85/C-04577), chloroorganics (according to ISO/DIS 15680), chlorobenzenes (according to ISO/DIS 15680), PAHs (according to ISO/DIS 17993) and PCBs (according to EPA GC 872A) were carried out. The analyses of these hazardous compounds were done in Department of Analytical Chemistry, Faculty of Chemistry, Gdańsk University of Technology.

## Results and Discussion

### Organic Substance Removal

In single- (series 1) and two-stage systems (series 2), removal effectiveness of organic substrates (COD and  $BOD_5$ ) was analyzed. The data showed that removal efficiency of organics measured as COD in series 1 was 49% (SBR 1 N-D) (HRT 3d) and 48% (SBR 2 N-D) (HRT 2d), which corresponds to COD in the effluent 349 and 356  $mgO_2/dm^3$ , respectively. In the effluent from SBR-D (series 2), COD was 384  $mgO_2/dm^3$  and the removal organics efficiency – 49%. Organic substances ( $BOD_5$ ) in the effluent in both systems was not higher than 8  $mgO_2/dm^3$ . The low COD removal effectiveness achieved in the experiments is in agreement with the low  $BOD_5/COD$  ratio of the untreated leachate. The poor biodegradability of the organics is typical for leachates from landfills in the methanogenic phase, which contains mainly refractory substances.

### Removal of Hazardous Compounds

In series 1 and 2 chloroorganics and chlorobenzenes in the effluent were not detected (Tab. 3). The concentrations of BTEX (as a sum of compounds) were 1.6  $\mu g/dm^3$

Table 3. Concentration of hazardous organics in raw leachate and in the effluent from single- and two-stage SBR systems.

Specific organics	Raw leachate (influent)	Single SBR system (effluent)	Two-stage SBR system (effluent)
BTEX ( $\mu\text{g}/\text{dm}^3$ )	175.8	1.6	0.8
Chloroorganics ( $\mu\text{g}/\text{dm}^3$ )	55.7	n.d.	n.d.
Chlorobenzenes ( $\mu\text{g}/\text{dm}^3$ )	0.75	n.d.	n.d.
PAHs ( $\mu\text{g}/\text{dm}^3$ )	1.97	0.793	0.377
PCBs ( $\mu\text{g}/\text{dm}^3$ )	0.001	0.001	0.001

n.d. - not detected

(single SBR system) and  $0.8 \mu\text{g}/\text{dm}^3$  (two-stage SBR system), which responds to removal effectiveness over 99%. The effluent contained PAHs on the level of  $0.793 \mu\text{g}/\text{dm}^3$  in single system and  $0.377 \mu\text{g}/\text{dm}^3$  in two-stage system. PCBs concentrations both in the effluent and in the influent remained on the same level –  $0.001 \mu\text{g}/\text{dm}^3$  (Tab. 3).

Principal removal mechanisms of analyzed chemicals are sorption onto activated sludge, volatilization, stripping due to the forced injection of air into mixed liquor and biodegradation. Removal efficiency of individual compounds diversifies and depends on substantial properties, especially their solubility, vapour pressure, chemical partitioning between phases and polarity correlated with the octanol-water partition coefficient  $K_{ow}$ .

Figure 3 presents benzene, toluene, ethylbenzene and xylene concentrations in the effluent from single and two-stage systems. Benzene and toluene contents in the effluent from SBR-D (two-stage system) were almost 3-fold lower, as for xylene concentration 1.25-fold lower in comparison to effluent from SBR 2 N-D (single system). Ethylbenzene concentration in both series was identical ( $0.1 \mu\text{g}/\text{dm}^3$ ). Results showed that in single system the lowest removal efficiency - 50% - was achieved for benzene. Toluene removal effectiveness was higher (97.8%) as for ethylbenzene and xylene (99%). In two-stage system removal effectiveness of all analyzed compounds (benzene, toluene, ethylbenzene and xylene) exceeded 99%.

Byrns [26] presented a theoretical model describing the likely distribution and fate for non-polar organic compounds in wastewater treatment systems. It follows that volatilization is a dominant mechanism removal of BTEX from activated sludge. Theoretically, the efficiency calculated on the basis of the model was 63.8% for benzene, 63.6% for toluene and 78.2% for xylene. Only a small amount of BTEX (ok. 3%) can be adsorbed to surplus sludge. Similarly, the basis mechanism of chloroorganics removal is volatilization, but the removal effectiveness of individual components is diverse. From the model it results that the highest volatilization – 91.4% should be observed for dichloroethene, the lowest one – 38.6% for dichloromethane. In contrary, PAHs indicate high ability to adsorption. Theoretical removal efficiency of acenaphthene, anthracene, pyrene and B(a)P, determined by the author should be 61.47%, 79.96%, 92.79% and 95.68%, respectively.

In our experiment removal the effectiveness of BTEX was higher than that calculated by Byrns's [26]. It could indicate that, besides volatilization, biodegradation occurred in activated sludge. BTEX biodegradation in mixed bacterial cultures was confirmed by Bielefeldt and Stensel [27]. Obtained by the authors, degradation rates for benzene, toluene, ethylbenzene and xylene were 0.24, 0.27, 0.27 and  $0.09 \text{ mg}/\text{mg}\cdot\text{d}$ , respectively. From the studies of Shim, Yang [28] in the fibrous-bed bioreactor containing the coculture of *Pseudomonas putida* and *Pseudomonas fluorescens* result that BTEX degradation rate depends on the concentration of organic compounds. At the concentrations  $135 \text{ mg}/\text{dm}^3$  (benzene),  $542 \text{ mg}/\text{dm}^3$  (toluene),  $186 \text{ mg}/\text{dm}^3$  (ethylbenzene) and  $212 \text{ mg}/\text{dm}^3$  (o-xylene) obtained by the authors' biodegradation rate constants for benzene and toluene were almost identical  $6.5 \cdot 10^{-3} \text{ h}^{-1}$  and  $6.6 \cdot 10^{-3} \text{ h}^{-1}$ , and lower for ethylbenzene –  $1.6 \cdot 10^{-3} \text{ h}^{-1}$  and xylene –  $3.7 \cdot 10^{-3} \text{ h}^{-1}$ .

It was found that the highest differences in PAH concentrations in the effluents from single- and two-stage systems were observed for naphthalene, acenaphthene, fluorene, phenanthrene and benzo(b)fluoranthene (Fig. 4). The effluent in both series did not contain indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene. The principal removal mechanism for these compounds is through sorption to sludge particles [26]. The compounds with a strong hydrophobic character are, in general, slowly biodegradable. Nevertheless, we cannot exclude partial or even complete

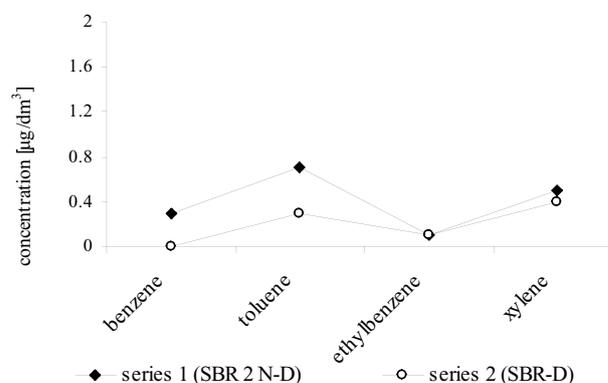


Fig. 3. BTEX concentration in the effluent from single SBR system (series 1, SBR 2 N-D) and two-stage SBR system (series 2, SBR-D).

mineralization of some of these compounds through processing in SBR. Klinge et al., [29] showed that the addition of sludge to soil markedly enhanced the mineralization of pyrene. The total mineralization of [ $^{14}\text{C}$ ]pyrene after 80 days corresponded to 23.6% of the added  $^{14}\text{C}$ .

In experiments in both systems total chloroorganics and chlorobenzenes elimination from leachate was observed. Topping [30] found in laboratory experiments that although 30% of 1,4-dichlorobenzene in a sewage effluent was sorbed onto solids during primary settling, more than 95% of the remainder would biodegrade during an aeration stage of activated sludge treatment. Other workers have also identified *Pseudomonas* bacteria capable of degrading 1,4-dichlorobenzene in activated sludge [31]. Kirk et al., [32] in the laboratory pilot plant study carried out over a 32-day period showed that all the chlorobenzenes were removed to a varying extent with overall percentage removals as follows: 1,4-dichlorobenzene 80%, 1,3-dichlorobenzene 77%, 1,2-dichlorobenzene 66%, heksachlorobenzene 63%, 1,2,4-trichlorobenzene 62%, 1,2,4,5-tetrachlorobenzene 33%, 1,2,3-trichlorobenzene 27% and 1,3,5-trichlorobenzene 25%.

### Nitrogen Removal

In a single activated sludge system the effect of leachate retention time (HRT) on nitrogen removal from leachate was investigated at methanol dosage (8 gCOD/g  $\text{N}_{\text{NO}_3}$ ).

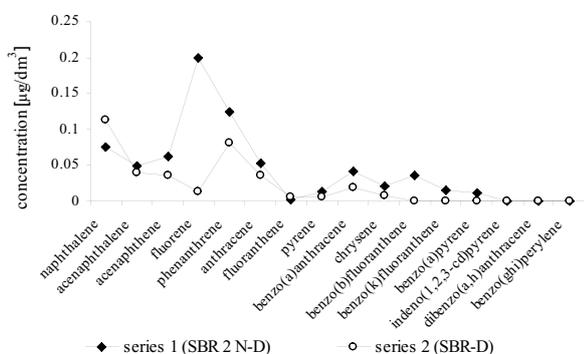


Fig. 4. PAHs concentrations in the effluent from single SBR system (series 1, SBR 2 N-D) and two-stage SBR system (series 2, SBR -D).

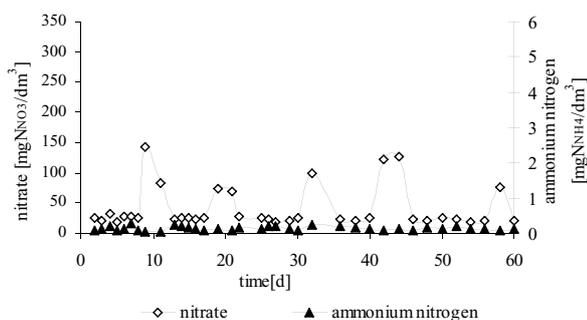


Fig. 5. Concentration of ammonium nitrogen and nitrate in the effluent from single SBR system (SBR 1 N-D; HRT 3d).

It is shown that the retention time influenced nitrogen concentration and its form in the effluent:

- in SBR 1 N-D (HRT 3d) total ammonium nitrogen elimination from leachate was achieved. Its concentration was approximately  $0.15 \text{ mgN}_{\text{NH}_4}/\text{dm}^3$ . However, complete denitrification was not obtained. Nitrate concentration was about  $23.5 \text{ mgN}_{\text{NO}_3}/\text{dm}^3$ , but sporadically nitrate contents in the effluent was on the level of  $143 \text{ mg N}_{\text{NO}_3}/\text{dm}^3$  (Fig. 5). Nitrite accumulation was not observed during denitrification and its concentration in the effluent was low -  $0.59 \text{ mgN}_{\text{NO}_2}/\text{dm}^3$ . The average concentration of the Kjeldahl nitrogen and total nitrogen were  $23 \text{ mgN}/\text{dm}^3$  and  $47 \text{ mgN}/\text{dm}^3$ , respectively. When in the effluent nitrate concentration was high ( $143 \text{ mg N}_{\text{NO}_3}/\text{dm}^3$ ), we observed increased total nitrogen concentration to the level of  $166 \text{ mgN}/\text{dm}^3$ .
- in SBR 2 N-D (HRT 2d) nitrate concentration was  $2.79 \text{ mgN}_{\text{NO}_3}/\text{dm}^3$ , as for nitrite -  $1.17 \text{ mgN}_{\text{NO}_2}/\text{dm}^3$ . The average ammonium nitrogen concentration was  $0.35 \text{ mgN}_{\text{NH}_4}/\text{dm}^3$ , but from time to time a higher amount of ammonium in the effluent was observed and the obtained value was  $179 \text{ mgN}_{\text{NH}_4}/\text{dm}^3$  (Fig. 6). The concentration of Kjeldahl nitrogen and total nitrogen in the effluent were nearly on the same level ( $25 \text{ mgN}/\text{dm}^3$  and  $29 \text{ mgN}/\text{dm}^3$ , respectively). The exception to this was when in the effluent a high concentration of ammonium was observed.

When in the effluent a sudden increase in nitrate or ammonium concentrations was observed, simultaneously there was the increase in organics concentration. It is supposed that the reason for organic compound increase is the drop of methanol consumption by denitrifiers. Methanol loading applications must be controlled to match  $\text{NO}_x$  levels in-situ and avoid either a significant deficit or surplus situation, in order to maximize system performance, while at the same time minimizing the potential for inhibition of nitrification.

Azevedo [33] found that large increases in methanol loading resulted in excess “bleeding” of unused methanol from the anoxic reactors into the aerobic reactors, possibly causing inhibition of nitrification (presumably by heterotrophic competition for oxygen in the aerobic

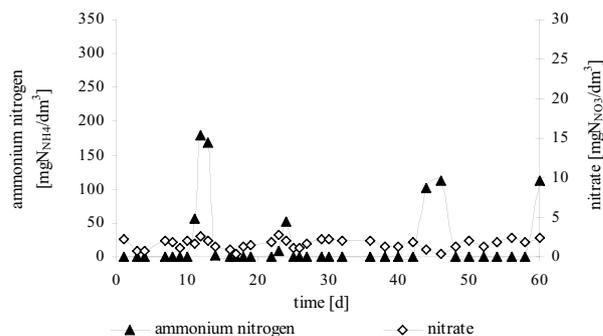


Fig. 6. Concentration of ammonium nitrogen and nitrate in the effluent from single SBR system (SBR 2 N-D; HRT 2d).

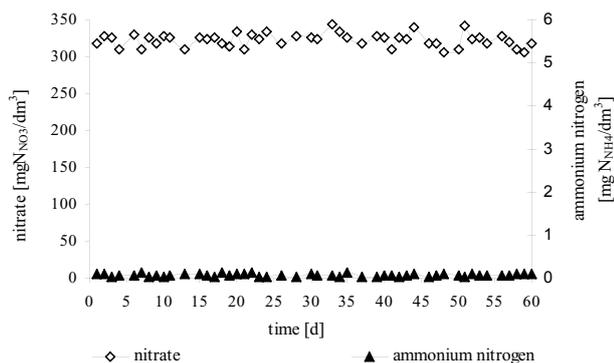


Fig. 7. Concentration of ammonium nitrogen and nitrate in the effluent from nitrifying tank (SBR-N) of two-stage SBR system.

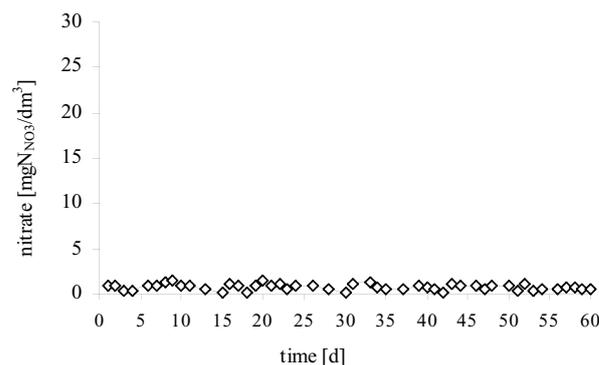


Fig. 8. Concentration of nitrate in the effluent from denitrifying tank (SBR-D) of two-stage SBR system.

reactors and/or methanol toxicity to *Nitrosomonas*). According to Loukidou, Zouboulis [16] in moving-bed biofilm SBR process with porous polyurethane as carrier material proper ratio of  $4 \text{ gCH}_3\text{OH}_{\text{added}}/\text{g N}_{\text{NO}_3}$  is necessary for complete denitrification. Lower than this optimum defined ratio may result in partial denitrification and, therefore, increase the concentrations of effluent  $\text{N}_{\text{NO}_3}$ . On the other hand, when the applied C/N ratio is higher than the optimum one, it will result in increased effluent concentrations of organic material and unnecessarily higher costs for further treatment [16].

In series 2 nitrogen removal in two-stage system, with separate nitrifying tank (SBR-N) and denitrifying tank (SBR-D) was investigated. In SBR-N nitrification process was conducted at the retention time 2d. The results showed that it was sufficient to achieve complete nitrification. It is confirmed by ammonium and nitrate concentrations in the effluent ( $0.08 \text{ mgN}_{\text{NH}_4}/\text{dm}^3$  and  $320 \text{ mgN}_{\text{NO}_3}/\text{dm}^3$ ) (Fig. 7). Nitrified leachate from SBR-N was next supplied to denitrifying reactor (SBR-D), where methanol was added in the amount of  $3.6 \text{ mg COD}/\text{mg N}_{\text{NO}_3}$ . In the system with post denitrification, methanol dose was sufficient to obtain complete nitrate reduction. The average nitrate concentration in the effluent did not exceed  $1 \text{ mg N}_{\text{NO}_3}/\text{dm}^3$ , and the process was highly stable (Fig. 8).

In two-stage system at the same leachate retention time (2d in SBR-N and 1d in SBR-D) total nitrogen elimination was achieved. In nitrifying tank ammonium concentration did not exceed  $0.08 \text{ mgN}_{\text{NH}_4}/\text{dm}^3$ , at leachate retention time 2d.

The same effluent quality -  $0.1 \text{ mg N}_{\text{NH}_4}/\text{dm}^3$  was obtained by Zaloum, Abott [34] at leachate retention time 3.2d but for anaerobic pretreatment leachate with four-fold lower ammonium concentration. For raw leachate with the contents of COD -  $12,760 \text{ mgO}_2/\text{dm}^3$  and TKN -  $218 \text{ mgN}/\text{dm}^3$  HTR should be lengthened to 20d.

According to Lo after Robinson and Carville [35] in SBR reactors (although favourable for nitrification N/COD ratio - 1.08) to obtain complete nitrification on the level of 99.8%, HRT should be no shorter than 20d.

In the effluent from denitrifying reactor (SBR-D)  $0.8 \text{ mg N}_{\text{NO}_3}/\text{dm}^3$  of nitrate concentration was observed and the denitrification process was highly stable. In two-stage system methanol demand for complete nitrogen elimination was  $3.6 \text{ mgCOD}/\text{mg N}_{\text{NO}_3}$ . In single system, at the same retention time and two-fold higher methanol dose nitrate concentration in the effluent was over  $20 \text{ mg N}_{\text{NO}_3}/\text{dm}^3$ .

## Conclusions

The results of organic and nitrogen compounds removal in activated sludge SBR reactors in single and two-stage system can be summarized as follows:

1. Removal efficiency of organic substances (COD and  $\text{BOD}_5$ ) was 49% and 93%, respectively, and was similar in both single and two-stage SBR systems.
2. During hazardous organic compound elimination the evident differences between tested systems were not observed. In the effluent from both systems chloroorganics and chlorobenzenes were not detected. The two-stage system seems to be more effective in case of the removal of some specific organics, especially BTEX and PAHs. Although in both tested systems removal effectiveness of mentioned compounds was relatively high, in the effluent from two-stage system sum of BTEX and PAH concentrations were two-fold lower than in single system effluent.
3. It can be concluded that in single system (at the same leachate retention time) methanol consumption was higher than in two-stage system. Process sensitivity and its low stability suggest that the dosage of external carbon source to single system should certainly be the most tricky parameter to control in a full scale process, especially when the nitrogen content in the leachate shows great variations. Too low dose in relation to the nitrate to be denitrified immediately results in the decrease in nitrogen removal, while an overdosage results in methanol remaining in the treated leachate and in an increase in COD and BOD discharge. Simultaneous nitrification and denitrification can be applied at

large treatment plants where full automation of dosing appliances is possible.

4. The efficiency of nitrogen removal from leachate was higher in two-stage system. At total leachate retention time 3d (nitrification - 2d HRT, denitrification - 1d HRT) and methanol dose 3.6 mgCOD/mg N<sub>NO3</sub> nitrogen removal effectiveness was 99.7%. In single system lower nitrogen removal efficiency (92.4%) was achieved at methanol dose 8 mgCOD/mg N<sub>NO3</sub>.

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